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Isochronal Annealing of Radiation Damage in α - and δ -Pu Alloys

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Magnetic isochronal annealing curves were measured on specimens of self damaged α -Pu and several δ -Pu alloys stabilized by Ga and Am. These results are compared to one another and to isochronal resistivity annealing curves, where distinct differences are observed between the magnetic and resistive annealing for the case of δ -Pu. The first stage of annealing observed in the resistivity measurements is largely missing from the magnetic measurements, indicating that interstitials contribute little if any signal to the magnetization, while the onset of vacancy migration is strongly reflected in the magnetization signal.

Introduction

Radiation damage is a naturally occurring process in all of the actinides, wherein the actinide atom spontaneously decays, creating a cascade of vacancies and interstitials that disorder the atomic lattice. In the case of Pu, the predominant route of decay is via a 5.16 MeV α -particle, which travels about 10 microns through the lattice losing about 99.9% of its energy through electronic excitations and atomic ionizations. Near the end of its travel, it begins to collide with atoms in the lattice and creates a cascade of about 800 nm in size with roughly 265 Frenkel pairs (an interstitial and a vacancy). Perhaps more interestingly, the resulting U ion recoils with 86 KeV of energy, travels about 12 nm, and initiates a dense cascade of vacancies and interstitials most of which anneal out over the succeeding few hundred picoseconds, leaving a cloud of approximately 2300 vacancies, interstitials, and their aggregates. Preliminary theoretical calculations suggested that these defects existed within a sphere of about 7.5 nm[1] diameter, while more recent calculations suggest a diameter closer to 30 nm[2]. This later value is consistent with estimations from experimental measurement of the saturation in the excess magnetic susceptibility arising from radiation damage[3]. Like Pu, Am also decays by α -emission, albeit with a slightly more energetic 5.28 MeV particle, which behaves in a manner substantially equivalent to the Pu case. The recoiling Np ion, with about 89 KeV of energy will also generate a damage cascade that to a first approximation mirrors that of the U ion for Pu. In the case of ^{243}Am , used in these experiments, the resulting ^{239}Np decays by a 720 KeV β^- emission, with a half-life of 2.35 days, to ^{239}Pu . The recoiling ^{239}Pu of the β^- emission has only a few eV of energy, and thus is unlikely to generate even one Frenkel pair, and the β^- lacks the momentum to create vacancy-interstitial pairs on its own.

At cryogenic temperatures, after the initial generation, the damage cascades are frozen in the lattice and the effects of these defects can be observed indirectly through the

measurement of many physical properties. The most frequently monitored physical property is resistivity because of the relative ease of the measurement, but similar observations can be made using heat capacity, dilatometry, thermal conductivity, or magnetization. Isochronal annealing studies of radiation damage map the change in a physical property as the radiation damage is thermally annealed by soaking for a fixed period at progressively higher temperatures, and then monitoring the physical property at a fixed low temperature. The basic protocol for a self-damaging specimen is to accumulate damage at a low temperature for a period of time, then measure the property of interest at that temperature, T_M . Then the specimen is heated to a higher temperature, held for a fixed period, and returned to T_M where the property is measured again. This process of heating, soaking, and returning to the base temperature is repeated at progressively higher annealing temperatures until the property of interest returns to its initial value indicating that all the radiation damage has been annealed away. Because these measurements are made on a self-damaging specimen, a first order correction to the annealing curve is made by repeating the above prescription on the same sample immediately after annealing. This allows for subtraction of the damage accumulated while the measurement is being performed. Further details of this process are described by Fluss et al elsewhere[4].

Method

Magnetization

Magnetization measurements reported were performed using a commercial magnetometer (Quantum Design MPMS 5) in an applied magnetic field of 3T. Small samples (15-90 mg) of the alloys were coated with a 5-micron layer of polyimide to contain spall and act as a layer of encapsulation. The samples were then mounted in the center of a 20 cm long brass sample tube and hermetically sealed with a gold O-ring under an inert atmosphere. The tube acts as a second level of encapsulation as well as helping to ensure the temperature of the sample is in equilibrium with the system thermometer. The magnetometer makes measurements using a second order gradiometer by moving the sample through a set of detection coils. Because the sample holder is much longer than the separation between the detection coils, its contribution to the magnetization is very small ($< 1\%$) and unaffected by radiation damage. Prior to loading a specimen, a background curve is run on the sample holder and this is subtracted from the sample measurement. An example of an uncorrected isochronal annealing curve and the first order correction curve are presented in Fig. 1 for a $\text{Pu}_{1-x}\text{Am}_x$ ($x=0.19$) alloy where the measured physical property was magnetization. The radiation damage was allowed to accumulate for 45 days at $T < 20$ K over which time the magnetization increased by about 6.5%. Magnetization measurements were made at 5K, and each annealing curve took approximately 6 days to complete, with soaks at each annealing temperature of 20 minutes.

Resistivity

Resistivity measurements were made on the same specimens measured via magnetization. The initial roughly spherical samples were rolled, with repeated intermediate annealing to remove strain until a thickness of ~ 75 microns was obtained. Then the samples were cut into a cloverleaf pattern and hermetically sealed inside of a

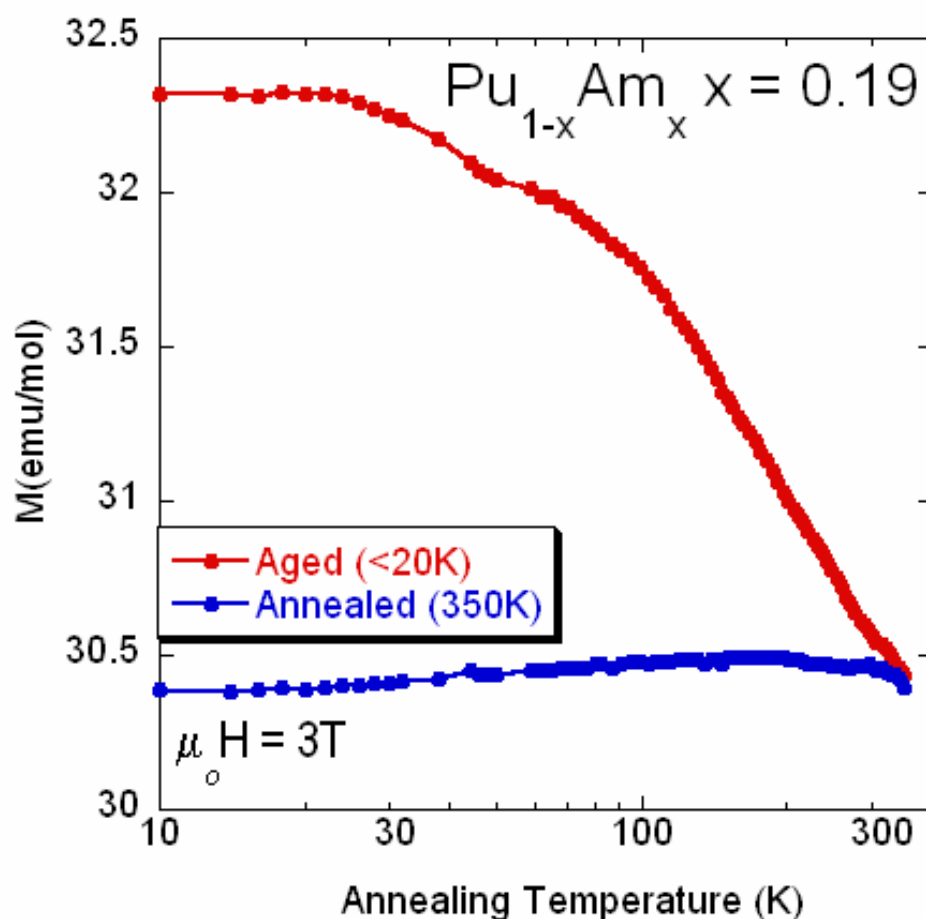


Fig 1 Uncorrected isochronal annealing data (red) and first order correction (blue) curve for a PuAm alloy. Radiation damage was accumulated for ~45 days on this specimen resulting in a 6.3% increase in the magnetization due to self-damage.

copper sample holder. Spring-loaded pins inside of the holder make contact with the sample, with two leads on each leaf of the pattern, totaling eight leads. In this configuration, both co-linear resistivity measurements and Van der Pauw configurations were available, as was the ability to make Hall measurements when placed in a magnetic field. The sample holder was then coated with polyimide to form a second layer of encapsulation. A thermometer (Cernox) is mounted inside of the sample holder, approximately 1-2 mm from the specimen. Measurements were made using a commercial system with a resistance bridge (Quantum Design PPMS).

Results and Discussion

While the effects of radiation damage are observable through the measurement of many different physical properties, the sensitivity of each property to such damage, and the specific type of damage may vary. This is very effectively demonstrated in Fig. 2, where isochronal annealing curves for α -Pu and δ -Pu(4.3at%Ga) are shown for both

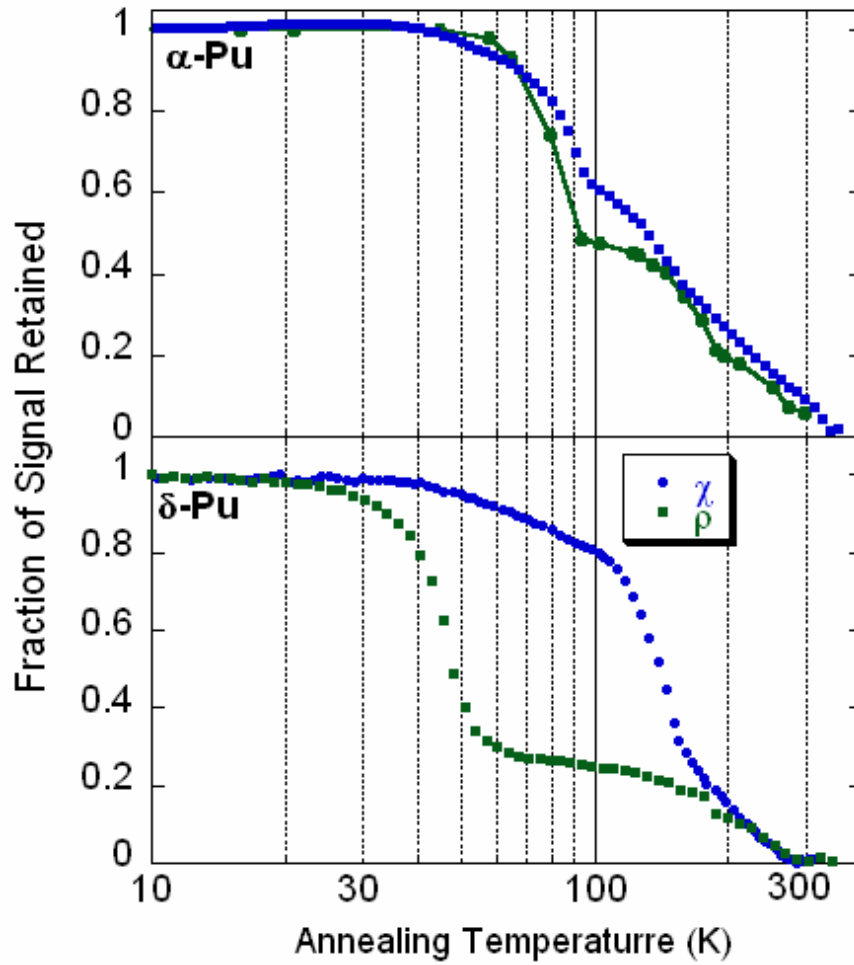


Fig. 2 Isochronal annealing curves for α -Pu and δ -Pu(4.3at%Ga) measured with magnetization (blue data) and resistivity (green data). The α -Pu resistivity data are from the work of Wigley[5] and track well with the magnetization data. For δ -Pu(4.3at%Ga), the first annealing stage observed in the resistivity is missing in the magnetization measurement, illustrating the different sensitivities of distinct measurement techniques to radiation damage.

resistivity and magnetization measurements. In the case of α -Pu, the two measurements track one another quite closely, both in terms of features and in terms of the signal retained. However, for the δ -Pu specimen, the magnetization annealing curve is largely insensitive to the first annealing stage, which is revealed quite clearly in the resistivity data, where roughly three-quarters of the damage signal is annealed away. This is where interstitials become mobile, and close vacancy-interstitial pairs annihilate. Isothermal resistivity measurements near 50K are second order as expected for a feature dominated by vacancy interstitial recombination as opposed to single impurity channels such as interstitials becoming trapped by an impurity, or reaching a grain boundary. The relative insensitivity of the magnetic measurement in this temperature range suggests that interstitials are largely invisible to the magnetic measurement in the case of δ -Pu. The magnetic annealing curve does show a strong reduction in signal at Stage III, which occurs around 150K in δ -Pu(4.3at%Ga) and is normally associated with vacancy migration. Here, roughly 60% of the magnetic signal is removed, while the impact on the resistivity is slight, indicating that the magnetic properties are strongly influenced by the

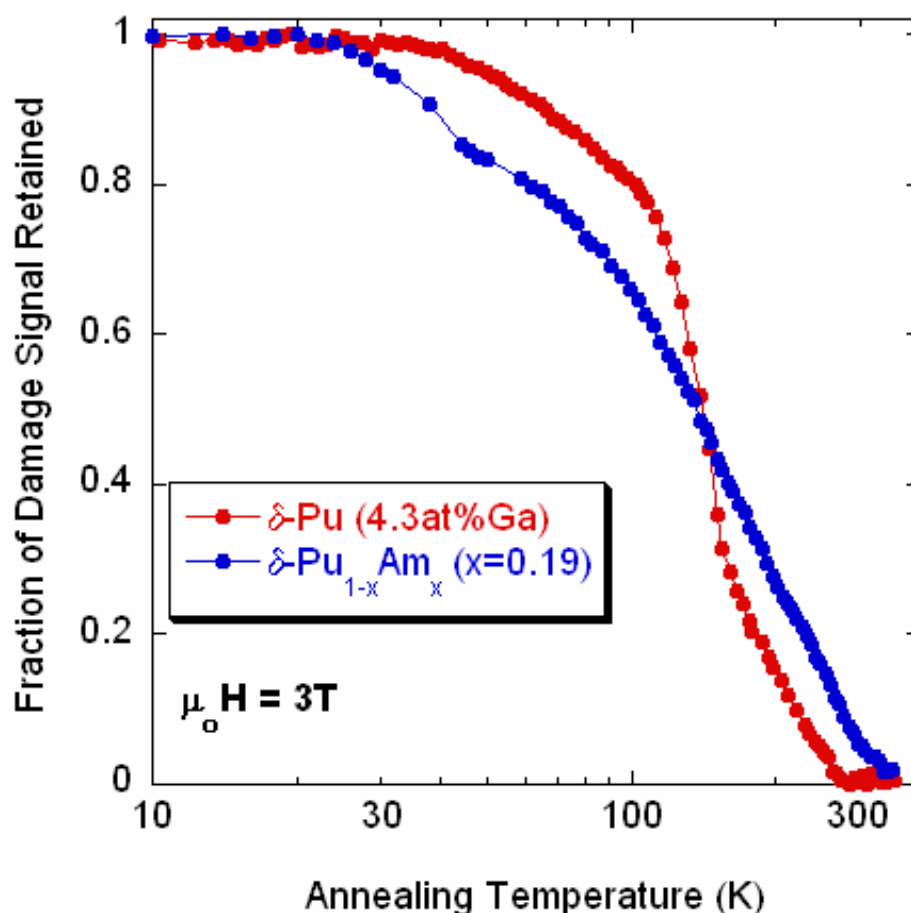


Fig 3 Isochronal magnetic annealing curves for two δ -Pu alloys. The general features are similar, although it appears that recovery begins at a slightly lower temperature for the expanded PuAm lattice and finishes at a slightly higher temperature.

vacancy concentration. Above this temperature, near 200 K, the fraction of the signal retained for both measurements overlaps again and follows a similar pattern to 300K, which is where the damage signal in this specimen anneals away. This overlap comprises stages IV and V of radiation damage recovery, typically involving release of vacancies from traps and finally the dissolution of vacancy clusters.

Fig. 3 shows the isochronal magnetic annealing curves for two stabilized δ -Pu alloys: the Ga stabilized specimen described above and a 19% Am disordered alloy, which remains FCC but has an expanded lattice relative to the Ga-stabilized alloy. In the dilute limit, the observed signal per α -decay is comparable in each specimen at 30-40 μ_B per α -particle. While the general features of the two annealing curves are similar, the onset of the first annealing stage occurs at a lower temperature in the Am alloy, suggesting that the interstitial migration energy decreases as the lattice expands. Similarly, the onset of stage III is considerably broadened relative to the δ -Pu(4.3at%Ga) specimen, becoming almost continuous with stage IV. This suggests that the migration energy of the vacancies varies with the local environment. Finally, full annealing in the PuAm alloy is about 50K higher than in the δ -Pu(4.3at%Ga) case. This may be a

reflection of the higher melting point of PuAm alloys, and suggests that an isochronal annealing study of americium will accumulate significantly more radiation damage at room temperature than plutonium.

Conclusions

Isochronal annealing studies of self-damage in Pu and Pu alloys show that different measurement techniques are sensitive to different damage products. Isothermal annealing measurements can extract the order and activation energies of the annealing stage. Because magnetization is very sensitive to stage III annealing, while resistivity is relatively insensitive, isothermal magnetic annealing may present an opportunity to obtain the vacancy migration energies in Ga stabilized δ -Pu. A comparison of isochronal annealing curves for δ -Pu alloys with different delta-gens may provide further insight into the mechanisms underlying radiation damage in these materials.

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References

- [1] W.G. Wolfer, "Radiation Effects in Plutonium," *Los Alamos Science*. **26**(1) 274 (2000).
- [2] A. Kubota, W. Wolfer, S. Valone, and M. Baskes, "Collision cascades in pure δ - plutonium," *Journal of Computer-Aided Materials Design*. **14**(3) 367 (2007).
- [3] S.K. McCall, M.J. Fluss, B.W. Chung, M.W. McElfresh, D.D. Jackson, and G.F. Chapline, "Emergent magnetic moments produced by self-damage in plutonium," *Proceedings of the National Academy of Sciences of the United States of America*. **103**(46) 17179 (2006).
- [4] M.J. Fluss, B.D. Wirth, M. Wall, T.E. Felter, M.J. Caturla, A. Kubota, and T.D. de la Rubia, "Temperature-dependent defect properties from ion-irradiation in Pu(Ga)," *Journal of Alloys & Compounds*. **368** 62 (2004).
- [5] D.A. Wigley, "Effect of annealing on the resistivity of self damaged plutonium," *Proceedings of the Royal Society of London, Series A: Mathematical and Physical Sciences*. **284** 344 (1964).